(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 276 793 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
01.08.2012 Bulletin 2012/31

(21) Application number: **09746148.7**

(22) Date of filing: **12.05.2009**

(51) Int Cl.:
C08G 75/04 *(2006.01)* ***C08L 81/02*** *(2006.01)*
C07F 7/18 *(2006.01)*

(86) International application number:
PCT/IB2009/005574

(87) International publication number:
WO 2009/138853 (19.11.2009 Gazette 2009/47)

(54) **SULFUR MODIFIED SILANES FOR THE ELABORATION OF HIGH REFRACTIVE INDEX MATERIALS**

SCHWEFELMODIFZIERTE SILANE ZUR HERSTELLUNG VON MATERIALIEN MIT HOHEM BRECHUNGSINDEX

SILANES MODIFIÉS PAR DU SOUFRE UTILISÉS POUR FABRIQUER DES MATIÈRES À INDICE DE RÉFRACTION ÉLEVÉ

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR

(30) Priority: **15.05.2008 US 121278**

(43) Date of publication of application:
26.01.2011 Bulletin 2011/04

(73) Proprietor: **Essilor International (Compagnie Générale d'Optique)**
94220 Charenton Le Pont (FR)

(72) Inventors:
- **BITEAU, John**
  33710 St Petersburg, Florida (US)
- **MOSSE, Herbert**
  33548 Lutz, Florida (US)

(74) Representative: **Salou, Clarisse et al**
Santarelli
14, avenue de la Grande-Armée
B.P. 237
75822 Paris Cedex 17 (FR)

(56) References cited:
EP-A- 1 785 458 **US-A- 4 366 307**

EP 2 276 793 B1

Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates generally to high refractive index materials, and processes for synthesizing them, and applications for using them as optical bulk materials or high index coatings which are preferably hard coatings.

[0002] For ophthalmic lenses, plastic materials represent a safer, thinner and lightweight alternative. Such plastic ophthalmic lenses frequently have a surface coating to provide scratch resistance or to impart functional optical features such as tints or anti-reflective surfaces.

[0003] Silane based matrices can be used for both coatings and bulk materials. These silanes have reasonably good mechanical properties, but suffer from relatively low refractive index (RI) values, between 1.42 and 1.55. As the demand for thinner and lighter lenses increases, there is a greater need for materials having a higher index of refraction and better mechanical properties. The eye lens industry is focusing on producing high index lenses (refractive index, about 1.6-1.7), which require correspondingly high refractive index (1.63-1.68) coatings. The refractive index of presently available organic coatings is about 1.5, making them unsuitable for high index lenses. Therefore, there is an immediate need for optical grade coatings that have high refractive index.

[0004] Plastic lens usually have refractive index as high as 1.67, 1.74 or even 1.80. Conventional coatings usually have a low refractive index of about 1.50. The large difference between the lens substrate refractive index and the coating refractive index causes unsightly fringes. Therefore, it would be desirable to have higher index coatings, and hybrid coatings with correspondingly improved mechanical properties. The document EP1785458 discloses transparent high refractive index optical coatings containing a polythiol compound, vinyl trimethoxysilanes and metal oxide particles.

[0005] One prior hybrid coating is disclosed in US Published Application 2005/0123771. An epoxy silane is hydrolyzed and combined with colloidal silica and an aluminum compound, like an aluminum chelate. The composition has application as an abrasion resistant coating and is useful when applied in conjunction with nonreflective coating layers. Another prior art example s described in US Published Application 2003/165698.

[0006] An example of prior art bulk materials is the class of organic polymers. Organic polymers based on thiols and thio-ethers provide a high refractive index (up to 1.70) but are purely organic and not hybrid organic-inorganic. Mechanical properties can be improved by introducing inorganic nanoparticles, however the resulting material is usually hazy due to nanoparticles aggregation.

[0007] Hybrid materials, such as transparent hybrid bulk materials are known to be made from silanes leading to an inorganic network. In that case the refractive index is low. The refractive index can be increased slightly by introducing metal alkoxides. However in this case huge differences in kinetics lead to precipitation of the metal alkoxide, limiting the per cent of metal alkoxide content or leading to hazy materials. A prior bulk material is disclosed in US Patent 6,624,237 by hydrolyzing an organo-silicon monomer. The monomer may be combined with an epoxy silane or photochromic compound before hydrolyzing. Another prior art example is described in WO94/25406, which discusses the sol-gel process.

[0008] An example of prior art silane coatings is glycidoxypropyltrimethoxysilane, which is referred to by the commercial name Glymo. Glymo is a precursor that is currently used for abrasion resistant coatings in the ophthalmic industry. A high crosslinking rate is achieved, but its refractive index is limited to 1.51. Higher refractive index coatings are obtained by adding high refractive index nanoparticles, such as TiO_2 or ZrO_2. Such coatings are limited in refractive index due to the low RI of the Glymo. When the content of high RI nanoparticles is increased the coatings becomes brittle and mechanical performance is reduced.

[0009] Accordingly, it is an object of the present invention to provide a new class of materials, and their applications as high refractive index bulk materials and coatings.

[0010] For the process embodiment of the invention, we propose:

(i) mixing a polythiol (I) and an alkenyl silane (II), to obtain or make a solution; and
(ii) exposing the solution to UV radiation or heat, preferably by UV radiation, to undergo thiol-ene addition thereby producing a polysulfide polysilane (III).

[0011] The mixing step (i) may comprise the addition before, during or after the mixing, of a further compound, which may be, for example, a catalyst, a photoinitiator, a solvent or combinations thereof. The photoinitiator is particularly useful for carrying out the further step (ii) by exposing the solution to UV radiation. The catalyst is particularly useful for carrying out the further step (ii) by exposing the solution to heat.

[0012] The polythiol (I) has a formula,

$$(HS)\text{-}R\text{-}(SH)_n,$$

wherein

- n is an integer comprised from 1 to 5 inclusive; and
- R is a group selected from:

  arylene,
  heteroarylene,
  and linear or branched (C_2 - C_{30}) alkylene, wherein from 1 to 10 carbon atoms may be replaced by a group selected from (CO), (SO_2), NR_4 where R_4 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S, or P; and/or each alkylene group may be optionally substituted by a group selected from hydroxyl, carboxy, aryl, and heteroaryl, these two last groups may be substituted onto the said alkylene chain at a terminal position or inside the alkylene chain.

[0013] The alkenyl silane (II) has the formula

$$(R_1)_mX_{(3-m)}Si\text{-}R_2\text{-}R_3$$

wherein:

- R_1 is a linear or branched (C_1-C_{10}) alkyl group, which comprised optionally from 1 to 5 heteroatoms selected from NR_6 where R_6 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S, or P; and/or each alkyl group may be optionally substituted by a group selected from hydroxyl, carboxy, and (C_1-C_6) alkoxy;
- X is a group selected from a halogen atom, and -OR_5, wherein R_5 represents a group selected from (C_3-C_{10}) cycloalkyl, (C_3-C_{10}) heterocycloalkyl, and linear or branched (C_1-C_6) alkyl which may be comprised from 1 to 3 heteroatoms selected from the group consisting of NR_7 where R_7 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O or S; and/or each alkyl group may be substituted by a group selected from linear or branched (C_1-C_6) alkoxy, carboxy, and hydroxy;
- m is an integer comprised from 0 to 2 inclusive;
- R_2 is either absent or represented by a group selected from linear or branched (C_2-C_{10}) alkylene wherein from 1 to 4 carbon atom may be replaced by a group selected from (CO), NR_8, where R_8 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O or S; and/or each alkylene group may be optionally substituted by a group selected from linear or branched (C_1-C_6) alkoxy, carboxy, and hydroxy;
- R_3 represents a group selected from linear or branched (C_2-C_{10}) alkenyl, (C_4-C_{10}) cycloalkenyl, and (C_4-C_{10}) heterocycloalkenyl, each of these groups may be optionally substituted by a group selected from linear or branched (C_1-C_6) alkyl, linear or branched (C_1-C_6) alkoxy, linear or branched (C_1-C_6) thioalkoxy, carboxy, thiol, and hydroxyl.

[0014] In the present application the following definitions apply:

Aryl means monocyclic or polycyclic aromatic group which comprise usually from 4 to 14 carbon atoms and is optionally substituted by a group selected from hydroxy, linear or branched (C_1-C_6) alkyl, linear or branched (C_1-C_6) alkoxy, and carboxy. In accord with this meaning, the following aryl group could be mentioned, for example, phenyl, naphtyl, acenaphtenyl, biphenylenyl, anthracyl. According to the invention, the preferred aryl group represents a phenyl group.
Arylene means monocyclic or polycyclic aromatic group which comprise usually from 4 to 14 carbon atoms and an unsaturated double bond.
Heteroaryl means an aryl group as defined hereinbefore and wherein at least one carbon atom, and preferentially from 1 to 4 carbon atom, of the monocyclic or polycyclic is replaced by an heteroatom selected from O, N, and S. In accord with this meaning the following heteroaryl could be mentioned, for example, pyrymidyl, furyle, thienyl, thiadiazolyl, oxadiazolyl.
Halogen atom means an atom selected from Cl, Br, F and I.
Heteroarylene means an aryl group as defined hereinbefore and wherein at least one carbon atom, and preferentially from 1 to 4 carbon atom, of the monocyclic or polycyclic is replaced by an heteroatom selected from O, N, and S.
Alkylene means alkyl group which comprises an unsaturated double bond.
Alkenyl means alkyl group which comprises an unsaturated triple bond.

[0015] In the definition of compounds of formula (I) and (II), when it is mentioned that a group may be "substituted", it may be understood that in preferred embodiments such a group comprises from 1 to 4 substituents.
[0016] The synthesized polysulfide polysilanes (III), obtained by thiol-ene addition, possesses generally a refractive index in the range comprises from 1.47 to 1.55.
[0017] For the product embodiment of the invention, we propose a polysulfide polysilane for the elaboration of high

refractive index materials, said polysulfide polysilane being synthesized as the reaction product of a polythiol (I) and an alkenyl silane (II).

[0018] These and other aspects, features and advantages of the present invention will be described or become apparent from the following detailed description of preferred embodiments.

[0019] As an overview of the new compound, a polythiol reactant is combined with an alkenylsilane reactant to provide a high index precursor material, which we refer to as polysulfide polysilane. The polysulfide polysilane is characterized by its preparation process. However the invention encompasses also the polysulfide polysilane of the invention if prepared by another preparation process. Thus the polysulfide polysilane is obtainable by the process according to the invention, and preferably is obtained by said process.

[0020] The polythiol (I) may be selected from the following, usually commercially available, compounds: 1,2-ethanedithiol; 1,3-propanedithiol; 1,4-butanedithiol; 1,2-butanedithiol; 1,5-pentanedithiol; 1,6-hexanedithiol; 1,8-octanedithiol; 2,2'-oxydiethanethiol; 3,6-dioxa-1,8-octanedithiol; ethylene glycol bisthiol-glycolate; dl-1,4-dithiothreitol; 2,2'-thiodiethanethiol; bis(2-mercaptoethyl)sulphone; 2,5-dimercapto-1,3,4-thiadiazole; 5-({2-[(5-mercapto-1,3,4-thiadiazol-2-yl) thio]ethyl}thio)-1,3,4-thiadiazole-2-thiol; pentaerythritol tetra(2-mercaptoacetate); trimethylolpropane tris (3-mercaptopropionate); trimethylolpropane tris (2-mercaptoacetate); 1,4-benzenedithiol; 1,3-benzenedithiol; 3,4-dimercaptotoluene; 1,4-benzenedimethanethiol; 1,3-benzenedimethanethiol; 1,6-di(methanethiol)-3,4-dimethyl-phenyl; [3-(mercaptomethyl)-2,4,6-trimethylphenyl]methanethiol; 1,5-dimercaptonaphthalene; 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol; 5-[3-(5-mercapto-1,3,4-oxadiazol-2-yl)propyl]-1,3,4-oxadiazole-2-thiol; 2-mercaptoethyl sulfide; 1,3,5-triazine-2,4,6(1H, 3H, 5H)-trithione; and 2,3-bis[(2-mercaptoethyl)thio]-1-propanethiol; preferably selected from the group comprising trimethylolpropane tris (2-mercaptoacetate), 2-mercaptoethyl sulfide, 3,6-dioxa-1, 8-octanedithiol, ethylene glycol bisthiol-glycolate, 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (3-mercaptopropionate), and more preferably selected from the group comprising 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (2-mercaptoacetate).

[0021] More generally, preferred polythiols will be those that can be formed into polysulfide polysilanes having a high refractive index (RI), for example, those resulting in an RI of about 1.47 or greater, and more preferably above 1.55. Exemplary polythiols which produce generally such RI values are trimethylolpropane tris (2-mercaptoacetate), 2-mercaptoethyl sulfide, 3,6-dioxa-1, 8-octanedithiol, ethylene glycol bisthiol-glycolate, 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (3-mercaptopropionate).

[0022] In practical tests described in greater detail below, 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (2-mercaptoacetate) emerged as the most preferred polythiols.

[0023] The polythiols (I) preferably have from 2 to 4 thiol groups (inclusive).

[0024] In the polythiols, R comprises preferentially from 1 to 20 carbon atoms, and when a heteroatom is present in the R group, it is preferentially a sulfur atom. In a first embodiment of the polythiol, R comprises preferentially from 1 to 10 carbon atoms, and from 1 to 6 sulfur atoms. Then in a further embodiment, the compound of formula (I) has a high ratio of S atoms to C atoms (nS/nC) that is to say at least 1 over 4 (nS/nC =1/4). This means that in the preferred compound of formula (I), there is at least 1 sulfur atom for 4 carbon atoms. The compound of formula (I) has more preferably a ratio of S atoms to C atoms (nS/nC) of at least 1 over 2 and even more preferably a ratio of at least 7 over10.

[0025] In a non limiting embodiment, the alkenyl silane (II) is selected from the group comprising vinylphenylmethymethoxysilane, vinylphenylmethylchlorosilane, vinylphenyldiethoxysilane, vinylphenyldichlorosilane, 10-undecenyltrimethoxysilane, 10-undecenyltrichlorosilane, 10-undecenyldimethylchlorosilane , 7-octenyltrimethoxysilane, 7-octenyltrichlorosilane , 7-octenyldimethylchlorosilane, allyltrimethoxysilane, allyltriethoxysilane , allyltrichlorosilane , allylphenyldichlorosilane , allyloxyundecyltrimethoxysilane, allylmethyldichlorosilane , allyldimethylchlorosilane, allyldimethoxysilane, allyldichlorosilane, allyl(chloropropyl)dichlorosilane, allyl(chloromethyl)dimethylsilane , 3- (n-allylamino)propyltrimethoxysilane, butenyltriethoxysilane , butenylmethyldichlorosilane, 5-hexenyltrichlorosilane , 5-hexenyldimethylchlorosilane , hexenyltriethoxysilane , vinyltriisopropoxysilane, vinyltris(methoxypropoxy)silane, vinyltris(2-methoxyethoxy)silane , vinyltriphenoxysilane , vinyltrimethoxysilane , vinyltriethoxysilane , vinyltrichlorosilane, vinyltri-t-butoxysilane , vinyltriacetoxysilane , vinyloctyldichlorosilane , vinylmethyldimethoxysilane , vinylmethyldiethoxysilane , vinylmethyldichlorosilane , vinylmethyldiacetoxysilane , 3-cyclohexenyltrichlorosilane , [2-(3-cyclohexenyl)ethyl]triethoxysilane, 3-(trimethoxysilyl)propyl methacrylate, and preferably vinyltrimethoxysilane.

[0026] Preferred alkenyl silanes will be those that can form into polysulfide polysilanes having a high refractive (RI) index, for example, those resulting in an RI of about 1.47 or greater, and more preferably above 1.5. In a practical test described in greater detail below, vinyltrimethoxysilane emerged as a preferred silane since it provided a polysulfide polysilane having an RI of 1.509.

[0027] A preferred form of the alkenyl silane is where m is zero, X is an alkoxy group, and R_2 is absent or represents a (C_2-C_3) alkylene group.

[0028] The thiol-ene addition reaction may be carried out upon stoichiometric quantities of the reactants. Non-stoichiometric quantities can be employed. In general, excess quantities of alkenyl silane (II) may be utilized to maximize the yield of the thiol-ene addition. When an excess of alkenyl silane is used for the thiol-ene addition, the product of the

reaction may be purified or the reaction mixture used as is for hydrolysis.

[0029] An hydrolysis step addition may be performed according to the invention, either in a separate stage from the one or more thiol-ene addition stage reactions or in a single stage together with the thiol-ene addition, in a so-called "one pot reaction." The hydrolysis provides according to the invention a hydrolyzed product or a mixture of hydrolyzed compounds.

[0030] The thiol-ene addition can be carried out under normal atmospheric conditions, while an inert atmosphere is preferred. The thiol-ene addition can be carried out at room temperature (usually around 20 °C). Certain additions are exothermic, and it may be preferable to cool the solution.

[0031] Those skilled in the art are aware that the thiol-ene reaction can be initiated by one of several techniques. To facilitate the reaction, one may add a photoinitiator. Among conventional photoinitiators the following can be used: benzophenones, acetophenone derivatives like α-hydroxyalkylphenylketones, benzoin alkyl ethers, benzylketals, monoacylphosphine oxides, bisacylphosphine oxides. When used the photoinitiators are present in a low amount such as lower that 1 weight % of the solution, preferably lower than 0.05% and even more preferably lower than 0.02%. If the photoinitiator can increase the rate of reaction, it also tends to increase yellowing of the composition and thus leads to the need of purification after synthesis of the polysulfide polysilane. Thus preferably the thiol-ene reaction is conducted without any photoinitiator.

[0032] In some specific cases a solvent might optionally be used. In such cases the solvent used generally does not interact with the thiol-ene addition. The solvent is preferably a non protic solvent. Solvents comprising insaturations like carbon double bonds should generally be avoided. A solvent can be used when the two reactants (I) and (II) are not miscible and/or when one of these two reactants is solid at the temperature at which the reaction is taking place. An example of solvent which might be used optionally is tetrahydrofuran.

[0033] Accordingly, the invention also concerns a process for completely or partially hydrolyzing the polysulfide polysilane (III). This optionally includes hydrolyzing a blend of the polysulfide polysilane (III) with another different polysulfide polysilane (III) or other silane, preferably another different polysulfide polysilane (III), usually in the presence of an acidic aqueous solution or a basic aqueous solution. The use of an acidic aqueous solution is preferred for the hydrolysis, in order to better control and separate the hydrolysis and the condensation steps. This acidic solution may be an acidic water solution (HCl in H_2O). The resulting products from hydrolyzing with the various options discussed are also part of the present invention.

[0034] COATINGS - The polysulfide polysilane (III) can be hydrolyzed to form an optical coating. Prior to hydrolyzing, another polysulfide polysilane or silane such as Glymo may be mixed with said polysulfide polysilane (III).

[0035] Thus the invention also concerns a process as already described, wherein following the exposing step (ii), the process further comprises the step (iiia) of hydrolyzing the polysulfide polysilane (III), said hydrolysis being preferentially an acidic hydrolysis, for example an hydrolysis in the presence of HCl, to form an optical coating (IVa).

[0036] Thus the invention further concerns a process as already described, wherein following the exposing step (ii), the process further comprises the steps of:

mixing the polysulfide polysilane (III) with another silane selected from the group consisting of Glymo, another different polysulfide polysilane (III) and combinations thereof; and
hydrolyzing (iiib) the mixture to form an optical coating (IVb), said hydrolysis being preferentially an acidic hydrolysis.

[0037] Thus the hydrolyzed products of the invention with the optional addition of silanes such as Glymo before the hydrolysis or the optional addition of inorganic nanoparticles can form high refractive index coatings.

[0038] The hydrolysis and the coating manufacture is well known form the one skilled in the art, and is for example described in US 6 624 237. The process according to the invention can further comprise the step of adding nanoparticles made from inorganic oxide(s) to the optical coating (IVa) or (IVb), wherein the nanoparticles are comprised preferably from 20% to 80% of the weight of the optical coating (IVa) or (IVb). This results generally in an optical coating having a refractive index in the range from 1.59 to 1.67, or greater.

[0039] For example, after hydrolyzing, a colloid may be added. This colloid is used as a source of nanoparticles and may include an inorganic oxide selected from the group consisting of silicon dioxide (silica), aluminum oxide (alumina), antimony oxide, tin oxide, titanium oxide, zirconium oxide and mixtures of such inorganic oxides. The hydrolyzed material comprising nanoparticles may be used as a high index hard coat for optical products, such as lenses.

[0040] The inorganic oxide which constitutes the nanoparticles is preferably added to the hydrolyzed product in the form of a colloid. It is preferable that the inorganic oxide maintains a stable dispersion state in the matrix and/or a low haze level, therefore, the average size of such particles may range from 1 to 200 nanometers, preferably from 2 to 100 nanometers, and more preferably, from 5 to 50 nanometers.

[0041] Examples of the above inorganic oxide include SiO_2, Al_2O_3, SnO_2, Sb_2O_5, Ta_2O_5, CeO_2, La_2O_3, Fe_2O_3, ZnO, WO_3, ZrO_2, In_2O_3 and TiO_2 alone or by mixture of at least two of them.

[0042] The inorganic oxides have a refractive index of from 1.7 to 3.0, and more preferably may be a multi-component

oxide(s) including two or more compounds selected from the group consisting of TiO_2 (refractive index: 2.5-2.7), SiO_2 (refractive index: 1.5), ZrO_2 (refractive index: 2.2), SnO_2 (refractive index: 2.0), Ce_2O_3 (refractive index: 2.2), $BaTiO_3$ (refractive index: 2.4), Al_2O_3 (refractive index: 1.73), and Y_2O_3 (refractive index: 1.92). Said multi-component oxide(s) may be composed at adequate contents by their refractive index, and more preferably, at least one of TiO_2-ZrO_2-SnO_2, TiO_2-ZrO_2-SiO_2 and TiO_2-SnO_2-SiO_2 may be used. Preferred the multi-component oxide according to the invention is selected from the group consisting of Optolake 1120z(S-95-A8)® and Optolake 1130Z(S-7-A8)®, which both are TiO_2-ZrO_2-SiO_2 composites with core-shell structure.

[0043] The process includes preferably adding colloids in the form of nanoparticles of inorganic oxide(s) after the hydrolysis step. The resulting hydrolyzed coatings may include one or more polysulfide polysilane made according the invention; may include Glymo or other silanes; and may include colloids. A catalyst or a solvent can optionally be added to the coating. The applications include dip-coating, spin-coating, flow, fan-coating, spray coating and other lens coating techniques. Dip-coating and spin-coating are industrially cost effective and are the preferred techniques. After the coating is applied to a precursor of a lens (or lens substrate material), it is cured and crosslinked to form a solid, hard coat.

[0044] The coating may be applied to a wide variety of lens substrate materials (or substrates). The substrates may be selected from mineral glass and also organic glass made of, for example, polycarbonate, polyamide, polyimide, polysulfone, copolymers of polyethyleneterephthalate and polycarbonate, polyolefine, homopolymers and copolymers of diethylene glycol bis(allylcarbonate), homopolymers and copolymers of (meth)acrylic monomers, homopolymers and copolymers of thio(meth)acrylic monomers, homopolymers and copolymers of urethane, homopolymers and copolymers of thiourethane, epoxy homopolymers and copolymers, and episulfure homopolymers and copolymers.

[0045] Preferably, the substrate is an organic material, more preferably it is an organic lens. According to a preferred embodiment of the invention, the substrate is an optic glass or an optical lens which is selected from ophthalmic lens, ocular visor, and sight optical systems. In a preferred embodiment, the substrate is an ophthalmic lens which may be an afocal, a unifocal, a bifocal, a trifocal or a progressive lens. Each ophthalmic lens may be also transparent, solar, or photochromic. In such case, the substrate coated with the abrasion-resistant coating may be overcoated with classical properties enhancing coatings such as anti-reflecting coating and top coat. Anti-reflecting coatings and their methods of making are well known in the art. The top coat, typically a hydrophobic top coat, which in the finished optical article constitutes the outermost coating on the optical substrate, is intended for improving the dirty mark resistance of the finished optical article.

[0046] Preferred substrates according to the invention are transparent substrates having a refractive index not smaller than 1.50 and include, for example, those made of polycarbonates which have a refractive index of 1.50. Moreover, a number of resins have been proposed in many patent publications and laid-open applications for use as plastic lenses for glasses, including those lenses made of polyurethane resins, methacrylic polymers, acrylic polymers and combinations thereof. For instance, lenses made of urethane resins are ones which are obtained by thermally curing monomers MR-6, MR-7 and MR-8 (commercially available from Mitsui Toatsu Chemicals Inc.). Lenses made of methacrylic polymers are those obtained by radical polymerization of TS-26 monomer commercially available from Tokuyama Co., Ltd.). Likewise, lenses obtained by use of urethane reaction and vinyl polymerization are those obtained by polymerizing ML-3 monomer (commercially available from Mitsubishi Gas Chemical Co., Inc.). All these resins can be used as substrates.

[0047] The coating can be applied to either the convex surface or the concave surface of the lens, or both. The hard coat should preferably have a dry final thickness of from about 0.2 microns (μm) to about 10 microns (μm). The lens may be treated or contacted with a primer prior to application of the coating layer.

[0048] BULK MATERIALS - The inventions also concerns a process as described above, wherein following the exposing step (ii), the process further comprises the steps of:

- hydrolyzing (iv) the polysulfide polysilane (III); and
- concentrating and then heating the hydrolyzed material to form a bulk material (V),

[0049] More generally, the polysulfide polysilane (III) of the invention is transformed into a bulk material (or lens substrate material or substrate) in a process known by the one skilled in the art, and said bulk material is encompassed by the invention.

[0050] In a preferred embodiment, following said hydrolyzing step (iv), the process further comprises the step of adding a catalyst selected from the group comprising metal chelates and amines.

[0051] To form bulk materials, the hydrolyzed product is preferably subjected to a sol-gel process including evaporation and crosslinking during a carefully controlled heating step leading to a densified and transparent material suitable fo use as bulk materiall (or substrate for lens substrate material), for example as described in US Patent 6,624,237. In general for the one skilled in the art "concentration" has the same meaning than "evaporation". A typical method for fabricating transparent dense glasses based on silanes using the sol-gel route, may comprise the following steps: A) a complete hydrolysis of a solution containing one or a several silicon alkoxides is carried out in a solvent or a mixture of organic solvents of the alkoxide(s) by using an aqueous acidic solution; B) the organic solvent(s) and the residual alcohols are

removed, and the resulting solution is concentrated by distillation under primary vacuum conditions so as to obtain a viscous sol, having for example a concentration of 1-10 moles/l in silicon atoms; C) gelling and air drying or drying in an inert atmosphere are initiated at a temperature lower than 158° F (70° C); D) the glass may be annealed at a temperature lower than 932° F (500° C).

[0052] The bulk material manufacture is well known by the one skilled in the art, and is for example described in US 6,624,237.

[0053] As used in the present specification, the term sol means and includes a colloidal dispersion of finely divided solid inorganic inorganic oxide particles in an aqueous or an organic liquid.

[0054] In one embodiment, the sol is slowly evaporated at room temperature and atmospheric pressure for 2 hours (h) to several weeks, preferentially for 15h. Optionally the partial evaporation is conducted under reduced pressure. In another embodiment the sol or the gel is heated at a temperature between 104° F and 392° F (40°C and 200°C), preferentially between 104° F and 266° F (70°C and 130°C) for a time comprised between 30 minutes and 3 weeks, preferentially between 4h and 72h. Optionally a condensation catalyst is added to the hydrolyzed compound in order to accelerate the crosslinking process.

[0055] The RI of the bulk materials according to the invention is generally in the range of at least 1.6, and preferably at least 1.63. This bulk material is generally characterized by a high refractive index, excellent transparency and low density.

[0056] The invention also encompasses a polysulfide polysilane (III) obtainable by a process as disclosed above, and having preferably a refractive index in the range of 1.47 to 1.55.

[0057] The invention also encompasses an optical coating (IVa, IVb) obtained by hydrolyzing said polysulfide polysilane (III), preferably wherein the optical coating (IVa, IVb) includes nanoparticles made from inorganic oxide(s), preferably in the range of between 20% and 80% of the weight of the optical coating (IVa, IVb).

[0058] The invention also encompasses an optical article, preferably an optical lens, made from a lens substrate material and coated by said optical coating.

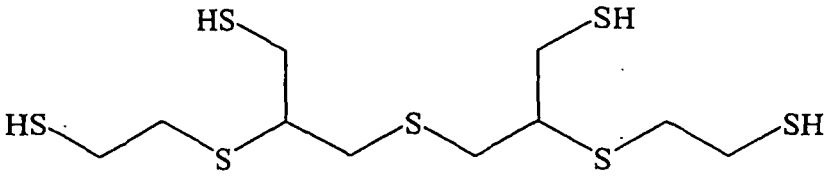
[0059] The invention also encompasses a bulk material (V) obtained by hydrolyzing, concentrating and then heating said polysulfide polysilane (III).

[0060] The invention also encompasses an optical article, preferably an optical lens, made from said bulk material (V).

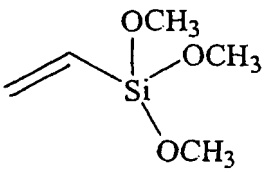
[0061] The process according to the invention will now be discussed in greater detail, by reference to the following examples.

Example 1

[0062] 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-Propanethiol (MR10B) and vinyltrimethoxysilane (VTMOS) were mixed together with tetrahydrofuran (THF) solvent to allow initial miscibility.

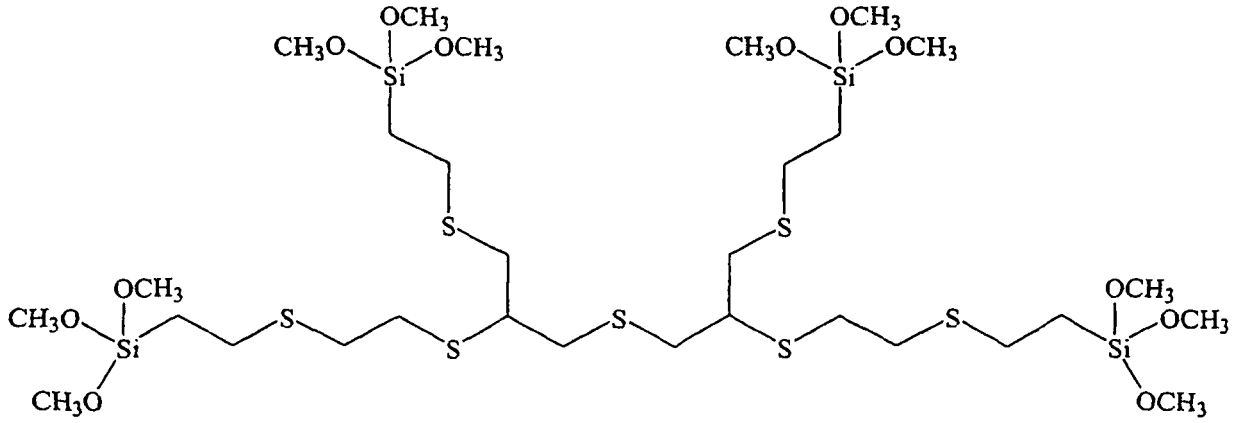


3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-Propanethiol



vinyltrimethoxysilane

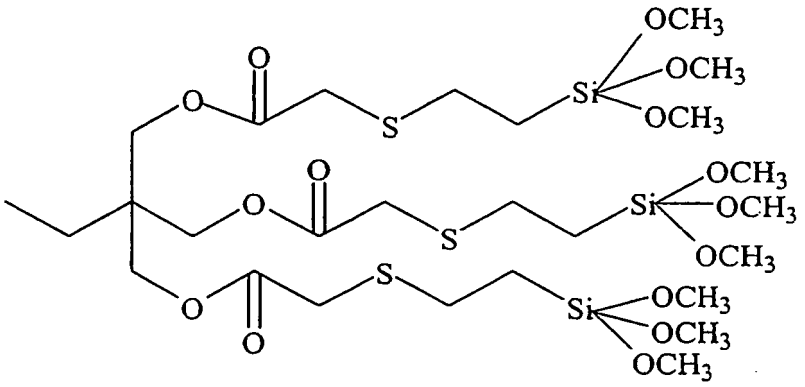
[0063] The solution was placed in a vial and exposed to UV irradiation. This represented one stoichiometric quantity of 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol, or MR10B, and four stoichiometric quantities of vinyltrimethoxysilane, or VTMOS. The thiol-ene addition took place under UV, without addition of any catalyst. The reaction product was as follows:



[0064] By weight, 13.23g MR10B, 12.45g VTMOS, and 4.32g THF were combined in a glass vial to produce approximately 30 grams of solution. The irradiation step consisted of five passes under the Fusion UV source (H Bulb), by a conveyor belt at 4.95 cm/s. The resulting polysulfide polysilane had a refractive index of 1.546.

Example 2

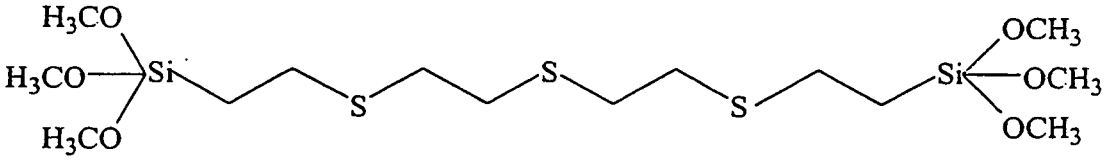
[0065] By weight, 35.65 g of trimethylolpropane tris (2-mercaptoacetate) and 44.47 g vinyltrimethoxysilane (VTMOS) were mixed together and subjected to UV radiation consisting of 5 passes under the Fusion UV source (H Bulb), on a conveyor belt at 4.95cm/s. The UV dose was 10.13 J/cm^2 at an intensity of 3.401 Watts/cm^2. A solvent was not necessary for miscibility of the VTMOS, but it could be optionally used. The resulting structure was:



[0066] The polysulfide polysilane produced had a refractive index of 1.477.

Example 3

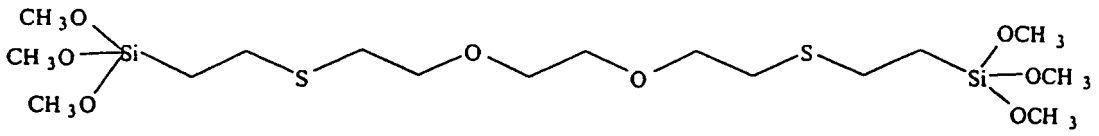
[0067] Under conditions similar to Example 2, 10 g of 2-Mercaptoethyl Sulfide was combined with 19.22 g of VTMOS to produce the following compound:



[0068] The compound had a refractive index of 1.509.

Example 4

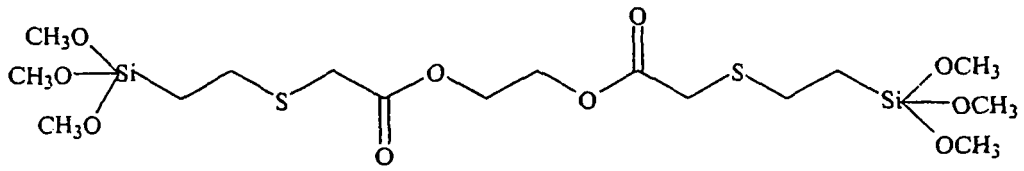
[0069] Under conditions similar to Example 2, 10 g of 3,6-Dioxa-1, 8-Octanedithiol was combined with 16.27 g of VTMOS to produce the following compound:



[0070] The compound had a refractive index of 1.460.

Example 5

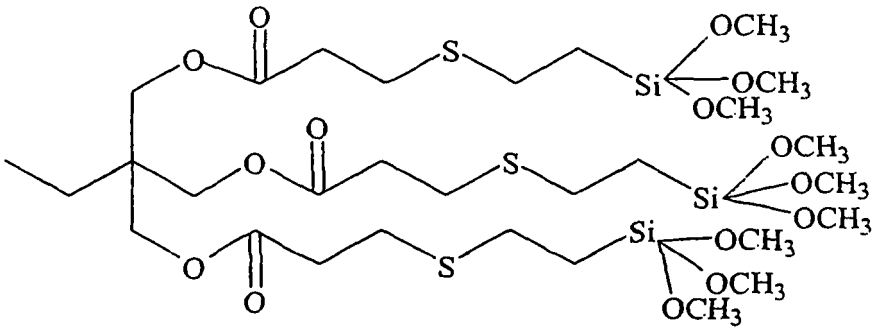
[0071] Under conditions similar to Example 2, 30 g of Ethylene Glycol Bisthiol-glycolate was combined with 42.23 g of VTMOS to produce the following compound:



[0072] The compound had a refractive index of 1.475.

Example 6

[0073] Under conditions similar to Example 2, 35.65 g of Trimethylolpropane tris (3-mercaptopropionate) was combined with 49.72 g of VTMOS to produce the following compound:



[0074] The compound had a refractive index of 1.480.

Example 7

[0075] The product obtained in Example 1 was hydrolyzed by acidic water solution (HCl in H_2O 1N). The sol-gel process took place under controlled conditions followed by a heating step, leading to a transparent material. The 2 steps cross-linking stage was made of a 1st step of 15h at room temperature followed by 3 days at 212° F (100°C). The bulk material obtained presented a refractive index equal to 1.63 and an Abbe value of 41. These 2 optical characteristics were measured by ellipsometry and by brewster angle definition (Metricon) at several wavelength of the visible. The density of this material was 1.38. Accordingly, high refractive index bulk hybrid organic-inorganic material could be formed by hydrolyzing heating the various polysulfide polysilanes to create a highly-crosslinked matrix. The resulting matrix was suitable for use in optical applications, for example lenses, for ophthalmic use.

[0076] The various polysulfide polysilanes obtained in the examples 1 to 6 were hydrolyzed to create coating formulations. The following examples were prepared with various types of colloidal nanoparticles oxides.

Coating Example 8

[0077] The formulation of a coating was made as follows: 20.64 grams of precursor 2 were mixed with 41.21 grams of methanol and stirred till the mixture became clear. 4.6 grams of HCl/H_2O (0.1N) were then added over 1 minute while stirring. Once the solution cleared 21.0 grams of methanol were immediately added. 29.3 grams of the colloid Optolake 1130Z(S-7-A8)® from Catalysts & Chemicals Ind. Co., Ltd. were then slowly added, followed by 3.24 grams of methyl-ethylketone. Finally, 0.01 grams of the surfactant EFKA 3034 were added to the solution.

Coating Examples 9-13

[0078] The formulation was the same as in example 8, but the polysulfide polysilane and the colloid were changed according to Table 1. Each coating is formulated based on 70% by weight of polysulfide polysilane before hydrolysis and 30% by weight of nanoparticles colloid from Catalyst & Chemicals Ind. Co., Ltd (excluding the dispersion medium of the colloid).

[0079] The coating solution was then deposited on lenses made from MR-8 (commercially available from Mitsui Toatsu Chemicals Inc.) by spin coating (for about 5 seconds at 500 rpm followed by 10s at 750 rpm). Once deposited on a lens the coating was cured at 212° F (100°C) for 3 hours.

[0080] Each coating is characterized, as reported in Table 1, by the refractive index of the matrix (cured in the same conditon) without colloid (column 5) and by the refractive index of the coating based on the polysulfide polysilane and the nanoparticles (column 6).

[0081] It should be understood that any combination of polysulfide polysilanes and colloids can be used together, and that Table 1 simply provides a limited number of exemplary combinations.

Table 1

Example	Example of polysulfide polysilane	TiO_2 based High Refractive Index Nanoparticles, from Catalyst & Chemicals Ind. Co., Ltd	RI of the polysulfide polysilane	RI of the matrix after hydrolysis-condensation	RI of a coating made of 70%wt matrix and 30%wt High Index Nanoparticles
8	2	1130Z(S-7-A8)	1.477	1.545	1.62
9	1	1120Z(11RU-7-A8)	1.546	1.630	1.67
10	3	1120Z(11RU-7-A8)	1.509	1.587	1.62
11	4	1120Z(11 RU-7-A8)	1.460	1.538	1.59
12	5	1120Z(11RU-7-A8)	1.475	1.538	1.59
13	6	1120Z(11RU-7-A8)	1.480	1.552	1.60

Coatings Examples 14, 15

[0082] Coatings 14 and 15 were formulated the same way as the examples 8 to 13. As reported in Table 2, the polysulfide polysilane from example 2 was used and various colloids from different suppliers. When not specified the supplier was Catalyst & Chemicals Ind. Co., Ltd.

[0083] The coatings 8, 9, 14 and 15 were also characterized with the Bayer abrasion test. The ASTM Bayer Abrasion resistant measurement was determined by measuring the percent haze of a coated and uncoated lens, before and after testing on an oscillating sand abrader as in ASTM F 735-81. The abrader was oscillated for 300 cycles with approximately 500 g of aluminum oxide (Al_2O_3) ZF 152412 supplied by Specially Ceramic Grains. The haze was measured using a Pacific Scientific Hazemeter model XL-211. The ratio of the uncoated lens haze (final-initial) was a measure of the performance of the coating, with a higher ratio meaning a higher abrasion resistance.

Table 2

Example	polysulfide polysilane from example	Refractive index (RI)		RI of Matrix + Nanoparticles	Colloid	Bayer abrasion test value
		polysulfide polysilanes	Matrix			
9	1	1.546	1.62	1.67	1120Z(11RU -7-A8))	~1
8	2	1.477	1.545	1.623	1130Z(S-7-A8)	~2.25
14	2	1.477	1.545	1.612	1120Z(S-95-A8)	~2
15	2	1.477	1.545	1.567	Novacentrix Al_2O_3	~1.5

[0084] The various Examples demonstrated that the hydrolyzed polysulfide polysilane materials could be further combined with colloids to form a high refractive index coating, which was suitable for coating onto optical articles, for example lenses, for ophthalmic use. The coatings presented herein could be a full or partial replacement for Glymo where a higher refractive index was desired.

[0085] In general, the higher refractive index coating would provide at least the following benefits:

Use a lower amount of expensive high refractive index colloids;
Provide a RI above 1.5, preferably above 1.59 and even more preferably above 1.67;
Use lower refractive index and cheaper colloids for the same refractive index;
Decrease the haze because of the need of less nanoparticles to reach a given refractive index; and
Decrease the haze by lowering the refractive index contrast between matrix and high index nanoparticles.

[0086] In conclusion, there have been described and shown two classes of reactants which could be combined pursuant to the thiol-ene addition reaction, the resulting polysulfide polysilanes (III) being characterized an hybrid organic-inorganic material that is highly transparent. The hybrid material usually combines excellent optical properties, such as low haze, with good mechanical properties.

Claims

1. A process for synthesizing a polysulfide polysilane (III), comprising the steps of:

(i) Mixing:

1) - a polythiol (I) represented by the general formula,

$$(HS)\text{-}R\text{-}(SH)_n \qquad (I)$$

wherein:

- n is an integer comprised from 1 to 5 inclusive; and
- R is a group selected from:

arylene
heteroarylene,
and linear or branched (C_2 - C_{30}) alkylene, wherein from 1 to 10 carbon atom may be replaced by a group selected from (CO), (SO_2), NR_4 where R_4 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S, and P; and/or each alkylene group may be optionally substituted by a group selected from hydroxyl, carboxy, aryl, and heteroaryl; and

2) an alkenyl silane (II) represented by the general formula

$$(R1)_mX_{(3-m)}Si\text{-}R_2\text{-}R_3 \qquad (II)$$

wherein:

- R1 is a linear or branched (C_1-C_{10}) alkyl group, which comprises optionally from 1 to 5 heteroatoms selected from NR_6 where R_6 represents a hydrogen atom or. linear or branched (C_1-C_6) alkyl, O, S, or P; and/or each alkyl group may be optionally substituted by a group selected from hydroxyl, carboxy, and (C_1-C_6) alkoxy;
- X is a group selected from a halogen atom, and -OR_5, wherein R_5 represents a group selected from (C_3-C_{10}) cycloalkyl, (C_3-C_{10}) heterocycloalkyl, and linear or branched (C_1-C_6) alkyl which may be comprised from 1 to 3 heteroatoms selected from the group consisting of NR_7 where R_7 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O, S; and/or each alkyl group may be substituted by a group selected from linear or branched (C_1-C_6)alkoxy, carboxy, and hydroxy;
- m is an integer comprised from 0 to 2 inclusive;
- R_2 is either absent or represented by a group selected from linear or branched (C_2-C_{10}) alkylene wherein from 1 to 4 carbon atoms may be replaced by a group selected from (CO), NR_8 where R_8 represents a hydrogen atom or linear or branched (C_1-C_6) alkyl, O or S; and/or each alkylene may be optionally substituted by a group selected from linear or branched (C_1-C_6) alkoxy, carboxy, and hydroxy;
- R_3 represents a group selected from linear or branched (C_2-C_{10}) alkenyl, (C_4-C_{10}) cycloalkenyl, and (C_4-C_{10}) heterocycloalkenyl, each of these groups may be optionally substituted by a group selected from linear or branched (C_1-C_6) alkyl, linear or branched (C_1-C_6) alkoxy, linear or branched (C_1-C_6) thioalkoxy, carboxy, thiol, and hydroxyl;

to obtain a solution ; and

(ii) exposing the solution to UV radiation or heat, preferably by UV radiation, to undergo thiol-ene addition thereby producing a polysulfide polysilane (III).

2. A process according to claim 1, wherein the polythiol (I) includes 2 to 4 thiol groups.

3. A process according to one of claims 1 or 2, wherein in the polythiol (I), R comprises from 1 to 20 carbon atoms, and when a heteroatom is present in the R group, it is a sulfur atom.

4. A process according to one of the claims 1 to 3, wherein in the polythiol (I), the ratio of S atoms to C atoms (nS/nC) is at least 1 over 4 preferably at least 1 over 2 and more preferably at least 7 over 10.

5. A process according to one of claims 1 to 4, wherein the polythiol (I) is selected from the group comprising 1,2-ethanedithiol; 1,3-propanedithiol; 1,4-butanedithiol; 1,2-butanedithiol; 1,5-pentanedithiol; 1,6-hexanedithiol; 1,8-octanedithiol; 2,2'-oxydiethanethiol; 3,6-dioxa-1,8-octanedithiol; ethylene glycol bisthiol-glycolate; dl-1,4-dithiothreitol; 2,2'-thiodiethanethiol; bis(2-mercaptoethyl)sulphone; 2,5-dimercapto-1,3,4-thiadiazole; 5-({2-[(5-mercapto-1,3,4-thiadiazol-2-yl)thio)ethyl}thio)-1,3,4-thiadiazole-2-thiol; pentaerythritol tetra(2-mercaptoacetate); trimethylolpropane tris (3-mercaptopropionate); trimethylolpropane tris (2-mercaptoacetate); 1,4-benzenedithiol; 1,3-benzenedithiol; 3,4-dimercaptotoluene; 1,4-benzenedimethanethiol; 1,3-benzenedimethanethiol; 1,6-di(methanethiol)-3,4-dimethyl-phenyl; [3-(mercaptomethyl)-2,4,6-trimethylphenyl)methanethiol; 1,5-dimercaptonaphthalene; 3,3'-thiobis [2-[(2-mercaptoethyl)thio)-1-propanethiol; 5-[3-(5-mercapto-1,3,4-oxadiazol-2-yl)propyl]-1,3,4-oxadiazole-2-thiol; 2-mercaptoethyl sulfide; 1,3,5-triazine-2,4,6(1H, 3H, 5H)-trithione; and 2,3-bis[(2-mercaptoethyl)thio]-1-propanethiol; preferably selected from the group comprising trimethylolpropane tris (2-mercaptoacetate), 2-mercaptoethyl sulfide, 3,6-dioxa-1, 8-octanedithiol, ethylene glycol bisthiol-glycolate, 3,3'-thiobis[2-[(2-mercaptoethyl)thio]-1-propanethiol and trimethylolpropane tris (3-mercaptopropionate), and more preferably selected from the group comprising 3,3'-thiobis[2-[(2-mercaptoethyl)thiol-1-propanethiol and trimethylolpropane tris (2-mercaptoacetate).

6. A process according to one of claims 1 to 5, wherein in the alkenyl silane (II) m is zero, X is an alkoxy group, and R_2 is absent or represents a (C_2-C_3) alkylene group.

7. A process according to one of claims 1 to 6, wherein the alkenyl silane (II) is selected from the group comprising vinylphenylmethymethoxysilane, vinylphenylmethylchlorosifane, vinylphenyldiethoxysilane , vinylphenyldichrorosilane, 10-undecenyltrimethoxysilane, 10-undecenyltrichlorosilane, 10-undecenyldimethylchlorosilane , 7-octenyltrimethoxysilane , 7-octenyltrichlorosilane, 7-octenyldimethylchlorosilane, allyltrimethoxysilane, allyltriethoxysilane , allyltrichlorosilane, allylphenyldichlorosilane , allyloxyundecyltrimethoxysilane , allylmethyldichlorosilane, allyld-

imethylchlorosilane, allyldimethoxysilane, allyldichlorosilane, allyl(chloropropyl)dichlorosilane, allyl(chloromethyl) dimethylsilane, 3- (n-allylamino)propyltrimethoxysilane, butenyltriethoxysilane , butenylmethyldichlorosilane , 5-hexenyltrichlorosilane , 5-hexenyldimethylchlorosilane , hexenyltriethoxysilane, vinyltriisopropoxysilane , vinyltris (methoxypropoxy)silane, vinyltris(2-methoxyethoxy)silane , vinyltriphenoxysilane, vinyltrimethoxysilane, vinyltriethoxysilane , vinyltrichlorosilane, vinyltri-t-butoxysilane, vinyltriacetoxysilane, vinyloctyldichlorosilane, vinylmethyldimethoxysilane , vinylmethyldiethoxysilane , vinylmethyldichlorosilane, vinylmethyldiacetoxysilane , 3-cyclohexenyltrichlorosilane, [2-(3-cyclohexenyl)ethyl]triethoxysilane, 3-(trimethoxysilyl)propyl methacrylate, and preferably vinyltrimethoxysilane.

8. A process according to one of claims 1 to 7, wherein following the exposing step (ii), the process further comprises the step (iiia) of hydrolyzing the polysulfide polysilane (III), said hydrolysis being preferentially an acidic hydrolysis, to form an optical coating (IVa).

9. A process according one of the claims 1 to 7, wherein following the exposing step (ii), the process further comprises the steps of:

mixing the polysulfide polysilane (III) with another silane selected from the group consisting of Glymo, another different polysulfide polysilane (III) and combinations thereof; and
hydrolyzing (iiib) the mixture to form an optical coating (IVb), said hydrolysis being preferentially an acidic hydrolysis.

10. A process according to one of claims 8 or 9, wherein following the hydrolyzing step (iiia) or (iiib), the process further comprises the step of adding nanoparticles made from inorganic oxide(s) to the optical coating (IVa) or (IVb), wherein the nanoparticles are comprised preferably from 20% to 80% of the weight of the optical coating (IVa) or (IVb).

11. A process according one of claims 1 to 7, wherein following the exposing step (ii), the process further comprises the steps of:

hydrolyzing (iv) the polysulfide polysilane (III); and
concentrating and then heating the hydrolyzed material to form a bulk material (V).

12. A process according to the preceding claim, wherein following said hydrolyzing step (iv), the process further comprises the step of adding a catalyst selected from the group comprising metal chelates and amines.

13. A polysulfide polysilane (III) obtainable by a process according to one of claims 1 to 12, and having preferable a refractive index in the range of 1.47 to 1.55.

14. An optical coating (IVa, IVb) obtained by hydrolyzing the polysulfide polysilane (III) of claim 13, preferably wherein the optical coating (IVa, IVb) includes nanoparticles made from inorganic oxide(s), preferably in the range of between 20% and 80% of the weight of the optical coating (IVa, IVb).

15. A bulk material (V) obtained by hydrolyzing, concentrating and then heating the polysulfide polysilane (III) of claim 14.

16. An optical article, preferably an optical lens, made from a lens substrate material and coated by an optical coating according to claim 14.

17. An optical article, preferably an optical lens, made from the bulk material (V) according to claim 15.

Patentansprüche

1. Verfahren für die Herstellung eines Polysulfid-Polysilans (III), umfassend die Schritte:

(i) Mischen:

1) - eines Polythiols (I), dargestellt durch die allgemeine Formel,

$$(HS)\text{-}R\text{-}(SH)_n \qquad (I)$$

bei welcher:

- n eine ganze Zahl ist, umfasst von 1 bis einschließlich 5; und
- R eine Gruppe ist ausgewählt aus:

Arylen
Heteroarylen,
und linearem oder verzweigtem (C_2-C_{30}) Alkylen, bei welchem 1 bis 10 Kohlenstoffatome durch eine Gruppe, ausgewählt aus (CO), (SO_2), NR_4, wobei R_4 ein Wasserstoffatom oder linear oder verzweigtes (C_1-C_6) Alkyl darstellt, O, S und P ersetzt werden können; und/oder jede Alkylengruppe optional durch eine Gruppe, ausgewählt aus Hydroxyl, Carboxy, Aryl und Heteroaryl substituiert werden kann, und
2) eines Alkenylsilans (II), dargestellt durch die allgemeine Formel

$$(R\text{-}1)_mX_{(3-m)}Si\text{-}R_2\text{-}R_3 \qquad (II)$$

bei welcher:

- R1 eine lineare oder verzweigte (C_1-C_{10}) Alkylgruppe ist, welche optional 1 bis 5 Heteroatome umfasst, ausgewählt aus NR_6, wobei R_6 ein Wasserstoffatom oder lineares oder verzweigtes (C_1-C_6) Alkyl darstellt, O, S oder P; und/oder jede Alkylgruppe optional durch eine Gruppe, ausgewählt aus Hydroxyl, Carboxy und (C_1-C_6) Alkoxy substituiert werden kann;
- X eine Gruppe ist, ausgewählt aus einem Halogenatom und -OR_5, wobei R_5 eine Gruppe darstellt, ausgewählt aus (C_3-C_{10}) Cycloalkyl, (C_3-C_{10}) Heterocycloalkyl und linearem oder verzweigtem (C_1-C_6) Alkyl, welches 1 bis 3 Heteroatome umfassen kann, ausgewählt aus der Gruppe bestehend aus NR_7, wobei R_7 ein Wasserstoffatom oder lineares oder verzweigtes (C_1-C_6) Alkyl darstellt, O, S; und/oder jede Alkylgruppe durch eine Gruppe, ausgewählt aus linearem oder verzweigtem (C_1-C_6) Alkoxy, Carboxy und Hydroxy substituiert sein kann;
- m eine ganze Zahl ist, umfasst von 0 bis einschließlich 2;
- R_2 entweder nicht vorhanden ist oder dargestellt ist durch eine Gruppe, ausgewählt aus linearem oder verzweigtem (C_2-C_{10}) Alkylen, wobei 1 bis 4 Kohlenstoffatome durch eine Gruppe, ausgewählt aus (CO), NR_8, wobei R_8 ein Wasserstoffatom oder lineares oder verzweigtes C_1-C_6 Alkyl darstellt, O oder S ersetzt werden können; und/oder jedes Alkylen optional durch eine Gruppe, ausgewählt aus linearem oder verzweigtem (C_1-C_6) Alkoxy, Carboxy und Hydroxy substituiert werden kann;
- R_3 eine Gruppe darstellt, ausgewählt aus linearem oder verzweigtem (C_2-C_{10}) Alkenyl, (C_4-C_{10}) Cycloalkenyl und (C_4-C_{10}) Heterocycloalkenyl, und jede von diesen Gruppen optional durch eine Gruppe, ausgewählt aus linearem oder verzweigtem (C_1-C_6) Alkyl, linearem oder verzweigtem (C_1-C_6) Alkoxy, linearem oder verzweigtem (C_1-C_6) Thioalkoxy, Carboxy, Thiol und Hydroxyl substituiert werden kann;

um eine Lösung zu erhalten; und

(ii) Exponieren der Lösung einer UV-Bestrahlung oder Hitze, vorzugsweise UV-Bestrahlung, damit sie Thiolen-Addition unterzogen wird und dabei ein Polysulfid-Polysilan (III) hergestellt wird.

2. Verfahren nach Anspruch 1, bei welchem das Polythiol (I) 2 bis 4 Thiolgruppen enthält.

3. Verfahren nach einem der Ansprüche 1 oder 2, bei welchem in dem Polythiol (I) R 1 bis 20 Kohlenstoffatome umfasst, und wenn ein Heteroatom in der R Gruppe vorhanden ist, es ein Schwefelatom ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, bei welchem in dem Polythiol (I) das Verhältnis von S Atomen zu C Atomen (nS/nC) mindestens 1 zu 4, vorzugsweise mindestens 1 zu 2 und noch bevorzugter mindestens 7 zu 10 ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, bei welchem das Polythiol (I) ausgewählt ist aus der Gruppe umfassend 1,2-Ethandithiol; 1,3-Propandithiol; 1,4-Butandithiol; 1,2-Butandithiol; 1,5-Pentandithiol; 1,6-Hexandithiol; 1,8-Octandithiol; 2,2'-Oxydiethanthiol; 3,6-Dioxa-1,8-Octandithiol; Ethylen-glycol-bisthiol-glycolat; D1-1,4-dithiothreitol; 2,2'-Thiodiethanthiol; Bis(2-mercaptoethyl)sulfon; 2,5-Dimercapto-1,3,4-thiadiazol; 5-({2-[(5-Mercapto-1,3,4-thiadiazol-2-y1)thio]ethyl}thio)-1,3,4-thiadiazol-2-thiol; Pentaerythritol-tetra(2-mercaptoacetat); Trimethylolpropan-tris (3-mercaptopropionat); Trimethylolpropan-tris(2-mercaptoacetat); 1,4-Benzendithiol; 1,3-Benzendithiol; 3,4-Dimer-

captotoluen; 1,4-Benzendimethanthiol; 1,3-Benzendimethanthiol; 1,6-Di(methanthiol)-3,4-dimethylphenyl; [3-(Mercaptomethyl)-2,4,6-trimethylphenyl]methanthiol; 1,5-Dimercaptonaphthalen; 3,3'-Thiobis[2-[(2-mercaptoethyl)thio]-1-propanthiol; 5-[3-(5-Mercapto-1,3,4-oxadiazol-2-yl)propyl]-1,3,4-oxadiazol-2-thiol; 2-Mercaptoethylsulfid; 1,3,5-Triazin-2,4,6(1H, 3H, 5H)-Trithion; und 2,3-Bis[(2-mercaptoethyl)thio]-1-propanthiol; bevorzugt ausgewählt aus der Gruppe umfassend Trimethylolpropan-tris-(2-mercaptoacetat), 2-Mercaptoethylsulfid, 3,6-Dioxa-1, 8-Octandithiol, Ethylen-glycol-bisthiol-glycolat, 3,3'Thiobis[2-[(2-mercaptoethyl)thio]-1-propanthiol und Trimethylolpropan-tris-(3-mercaptopropionat), und noch bevorzugter ausgewählt aus der Gruppe umfassend 3,3'-Thiobis[2-[(2-mercaptoethyl) thio]-1-propanthiol und Trimethylolpropan-tris-(2-mercaptoacetat).

6. Verfahren nach einem der Ansprüche 1 bis 5, bei welchem in dem Alkenylsilan (II) m Null ist, X eine Alkoxygruppe ist und R_2 nicht vorhanden ist oder eine (C_2-C_3) Alkylengruppe darstellt.

7. Verfahren nach einem der Ansprüche 1 bis 6, bei welchem das Alkenylsilan (II) ausgewählt ist aus der Gruppe umfassend Vinylphenylmethymethoxysilan, Vinylphenylmethylchlorosilan, Vinylphenyldiethoxysilan, Vinylphenyldichlorosilan, 10-Undecenyltrimethoxysilan, 10-Undecenyltrichlorosilan, 10-Undecenyldimethylchlorosilan, 7-Octenyltrimethoxysilan, 7-Octenyltrichlorosilan, 7-Octenyldimethylchlorosilan, Allyltrimethoxysilan, Allyltriethoxysilan, Allyltrichlorosilan, Allylphenyldichlorosilan, Allyloxyundecyltrimethoxysilan, Allylmethyldichlorosilan, Allyldimethylchlorosilan, Allyldimethoxysilan, Allyldichlorosilan, Allyl(chloropropyl)dichlorosilan, Allyl(chloromethyl)dimethylsilan, 3-(n-Allylamino)propyltrimethoxysilan, Butenyltriethoxysilan, Butenylmethyldichlorosilan, 5-Hexenyltrichlorosilan, 5-Hexenyldimethylchlorosilan, Hexenyltriethoxysilan, Vinyltriisopropoxysilan, Vinyltris(methoxypropoxy)silan, Vinyltris(2-methoxyethoxy)silan, Vinyltriphenoxysilan, Vinyltrimethoxysilan, Vinyltriethoxysilan, Vinyltrichlorosilan, Vinyltri-t-butoxysilan, Vinyltriacetoxysilan, Vinyloctyldichlorosilan, Vinylmethyldimethoxysilan, Vinylmethyldiethoxysilan, Vinylmethyldichlorosilan, Vinylmethyldiacetoxysilan, 3-Cyclohexenyltrichlorosilan, [2-(3-Cyclohexenyl)ethyl] triethoxysilan, 3-(Trimethoxysilyl)propyl-methacrylat, und bevorzugt Vinyltrimethoxysilan.

8. Verfahren nach einem der Ansprüche 1 bis 7, bei welchem nach dem Expositionsschritt (ii) das Verfahren weiterhin den Schritt (iiia) des Hydrolysierens des Polysulfid-Polysilans (III) umfasst, wobei die Hydrolyse vorzugsweise eine saure Hydrolyse ist, um eine optische Beschichtung (IVa) zu bilden.

9. Verfahren nach einem der Ansprüche 1 bis 7, bei welchem nach dem Expositionsschritt (ii) das Verfahren weiterhin die Schritte umfasst:

Mischen des Polysulfid-Polysilans (III) mit einem anderen Silan, ausgewählt aus der Gruppe bestehend aus Glymo, einem anderen verschiedenen Polysulfid-Polysilan (III) und Kombinationen davon; und
Hydrolysieren (iiib) der Mischung, um eine optische Beschichtung (IVb) zu bilden, wobei die Hydrolyse vorzugsweise eine saure Hydrolyse ist.

10. Verfahren nach einem der Ansprüche 8 oder 9, bei welchem nach dem Hydrolysierungsschritt (iiia) oder (iiib) das Verfahren weiterhin den Schritt der Zugabe von Nanopartikeln, die aus einem anorganischen Oxid oder anorganischen Oxiden hergestellt sind, zu der optischen Beschichtung (IVa) oder (IVb) umfasst, wobei die Nanopartikel vorzugsweise 20% bis 80% des Gewichts der optischen Beschichtung (IVa) oder (IVb) umfassen.

11. Verfahren nach einem Ansprüche 1 bis 7, bei welchem nach dem Expositionsschritt (ii) das Verfahren weiterhin die Schritte umfasst:

Hydrolysieren (iv) des Polysulfid-Polysilans (III); und
Konzentrieren und dann Erhitzen des hydrolysierten Materials, um ein Grundmaterial (V) zu bilden.

12. Verfahren nach dem vorhergehenden Anspruch, bei welchem nach dem Hydrolysierungsschritt (iv) das Verfahren weiterhin den Schritt der Zugabe eines Katalysators umfasst, ausgewählt aus der Gruppe umfassend Metallchelate und Amine.

13. Polysulfid-Polysilan (III), welches durch ein Verfahren nach einem der Ansprüche 1 bis 12 erhalten werden kann und vorzugsweise einen Brechungsindex in dem Bereich von 1,47 bis 1,55 hat.

14. Optische Beschichtung (IVa, IVb), welche durch Hydrolysieren des Polysulfid-Polysilans (III) aus Anspruch 13 erhalten wird, bei welcher vorzugsweise die optische Beschichtung (IVa, IVb) Nanopartikel enthält, die aus einem anorganischen Oxid oder anorganischen Oxiden hergestellt wurden, vorzugsweise in dem Bereich zwischen 20%

und 80% des Gewichts der optischen Beschichtung (IVa, IVb).

15. Grundmaterial (V), welches durch Hydrolysieren, Konzentrieren und dann Erhitzen des Polysulfid-Polysilans (III) aus Anspruch 14 erhalten wird.

16. Optischer Artikel, vorzugsweise eine optische Linse, welche aus einem Linsensubstratmaterial hergestellt und durch eine optische Beschichtung nach Anspruch 14 beschichtet wird.

17. Optischer Artikel, vorzugsweise eine optische Linse, welche aus dem Grundmaterial (V) nach Anspruch 15 hergestellt wird.

Revendications

1. Procédé pour synthétiser un polysulfure-polysilane (III), comprenant les étapes de :

(i) mélanger :

1) - un polythiol (I) représenté par la formule générale

$$(HS)\text{-}R\text{-}(SH)_n \qquad (I)$$

dans laquelle :

- n représente un nombre entier de 1 à 5 inclus ; et
- R représente un groupe choisi parmi :

arylène,
hétéroarylène,
et alkylène en C_2 à C_{30} linéaire ou ramifié, dans lequel 1 à 10 atomes de carbone peuvent être remplacés par un groupe choisi parmi les groupes (CO), (SO_2), NR_4, dans lequel R_4 représente un atome d'hydrogène ou un groupe alkyle en C_1 à C_6 linéaire ou ramifié, O, S et P ; et/ou chaque groupe alkylène peut être facultativement substitué par un groupe choisi parmi les groupes hydroxyle, carboxy, aryle et hétéroaryle ; et

2) un alcénylsilane (II) représenté par la formule générale

$$(R1)mX_{(3-m)}Si\text{-}R_2\text{-}R_3 \qquad (II)$$

dans laquelle :

- R_1 représente un groupe alkyle en C_1 à C_{10} linéaire ou ramifié, qui comprend facultativement 1 à 5 hétéroatomes choisis parmi NR_6, dans lequel R_6 représente un atome d'hydrogène ou un groupe alkyle en C_1 à C_6 linéaire ou ramifié, O, S et P ; et/ou chaque groupe alkyle peut être facultativement substitué par un groupe choisi parmi les groupes hydroxyle, carboxy et alkoxy en (C_1 à C_6) ;
- X représente un groupe choisi parmi un atome d'halogène et un groupe $-OR_5$, dans lequel R_5 représente un groupe choisi parmi les groupes cycloalkyle en C_3 à C_{10}, hétérocycloalkyle en C_3 à C_{10} et alkyle en C_1 à C_6 linéaire ou ramifié qui peut comprendre 1 à 3 hétéroatomes choisis dans le groupe consistant en NR_7, dans lequel R_7 représente un atome d'hydrogène ou un groupe alkyle en C_1 à C_6 linéaire ou ramifié, O et S ; et/ou chaque groupe alkyle peut être substitué par un groupe choisi parmi les groupes alkoxy en C_1 à C_6 linéaire ou ramifié, carboxy et hydroxy ;
- m représente un nombre entier de 0 à 2 inclus ;
- R_2 est absent ou bien est représenté par un groupe choisi parmi les groupes alkylène en C_2 à C_{10} linéaires ou ramifiés, dans lesquels 1 à 4 atomes de carbone peuvent être remplacés par un groupe choisi parmi les groupes (CO), NR_8, dans lequel R_8 représente un atome d'hydrogène ou un groupe alkyle en C_1 à C_6 linéaire ou ramifié, O ou S ; et/ou chaque groupe alkylène peut être facultativement substitué par un groupe choisi parmi les groupes alkoxy en C_1 à C_6 linéaire ou ramifié, carboxy et hydroxy ;
- R_3 représente un groupe choisi parmi les groupes alcényle en C_2 à C_{10} linéaire ou ramifié, cycloalcényle en C_4 à C_{10} et hétérocycloalcényle en C_4 à C_{10}, chacun de ces groupes peut être facultativement

substitué par un groupe choisi parmi les groupes alkyle en C_1 à C_6 linéaire ou ramifié, alkoxy en C_1 à C_6 linéaire ou ramifié, thioalkoxy en C_1 à C_6 linéaire ou ramifié, carboxy, thiol et hydroxyle ;

pour obtenir une solution ; et

(ii) exposer la solution à un rayonnement UV ou de la chaleur, de préférence par un rayonnement UV, pour subir une addition thiolène, en produisant ainsi un polysulfure-polysilane (III).

2. Procédé selon la revendication 1, dans lequel le polythiol (I) comprend 2 à 4 groupes thiol.

3. Procédé selon l'une des revendications 1 ou 2, dans lequel, dans le polythiol (I), R comprend 1 à 20 atomes de carbone et, lorsqu'un hétéroatome est présent dans le groupe R, il est un atome de soufre.

4. Procédé selon l'une des revendications 1 à 3, dans lequel, dans le polythiol (I), le rapport des atomes de S aux atomes de C (nS/nC) est d'au moins 1 sur 4, de préférence d'au moins 1 sur 2 et de façon plus préférée d'au moins 7 sur 10.

5. Procédé selon l'une des revendications 1 à 4, dans lequel le polythiol (I) est choisi dans le groupe comprenant le 1,2-éthanedithiol ; le 1,3-propanedithio ; le 1,4-butane-dithiol ; le 1,2-butanedithiol ; le 1,5-pentanedithiol ; le 1,6-hexane-dithiol ; le 1,8-octanedithiol ; le 2,2'-oxydiéthanethiol ; le 3,6-dioxa-1,8-octanedithiol ; le bisthiol-glycolate d'éthylèneglycol ; le dl-1,4-dithio-thréitol ; le 2,2'-thiodiéthanethiol ; la bis-(2-mercapto-éthyl)-sulfone ; le 2,5-dimercapto-1,3,4-thiadiazole ; le 5-({2-[(5-mercapto-1,3,4-thiadiazole-2-yl)thio]éthyl}thio)-1,3,4-thiadiazole-2-thiol ; le tétra-(2-mercaptoacétate) de pentaérythritol ; le tris-(3-mercaptopropionate) de triméthylolpropane ; le tris-(2-mercaptoacétate) de triméthylolpropane ; le 1,4-benzènedithiol ; le 1,3-benzènedithiol ; le 3,4-dimercapto-toluène ; le 1,4-benzènediméthanethiol ; le 1,3-benzène-diméthanethiol ; le 1,6-di(méthanethiol)-3,4-diméthyl-phényle ; le [3-(mercaptométhyl)-2,4,6-triméthylphényl]-méthanethiol ; le 1,5-dimercaptonaphtalène ; le 3,3'-thiobis-[2-[(2-mercaptoéthyl)thio]-1-propanethiol ; le 5-[3-(5-mercapto-1,3,4-oxadiazole-2-yl)propyl]-1,3,4-oxadiazole-2-thiol ; le sulfure de 2-mercaptoéthyle ; la 1,3,5-triazine-2,4,6-(1H,3H,5H)-trithione ; et le 2,3-bis-[(2-mercaptoéthyl)-thio]-1-propanethiol ; choisi de préférence dans le groupe comprenant le tris-(2-mercaptoacétate) de triméthylolpropane, le sulfure de 2-mercaptoéthyle, le 3,6-dioxa-1,8-octanedithiol, le bisthiol-glycolate d'éthylèneglycol, le 3,3'-thiobis-[2-[(2-mercaptoéthyl)thio]-1-propanethiol et le tris-(3-mercaptopropionate) de triméthylolpropane, et choisi de façon plus préférée dans le groupe comprenant le 3,3'-thiobis-[2-[(2-mercapto-éthyl)thio]-1-propanethiol et le tris-(2-mercaptoacétate) de triméthylolpropane.

6. Procédé selon l'une des revendications 1 à 5, dans lequel, dans l'alcénylsilane (II), m est égal à zéro, X représente un groupe alkoxy, et R_2 est absent ou représente un groupe alkylène en C_2 ou C_3.

7. Procédé selon l'une des revendications 1 à 6, dans lequel l'alcénylsilane (II) est choisi dans le groupe comprenant le vinylphénylméthyméthoxysilane, le vinyl-phénylméthylchlorosilane, le vinylphényldiéthoxysilane, le vinylphényl-dichlorosilane, le 10-undécényltriméthoxy-silane, le 10-undécényltrichlorosilane, le 10-undécényl-diméthylchlorosilane, le 7-octényltriméthoxysilane, le 7-octényltrichlorosilane, le 7-octényldiméthylchlorosilane, l'allyltriméthoxysilane, l'allyltriéthoxysilane, l'allyl-trichlorosilane, l'allylphényldichlorosilane, l'allyloxy-undécyltriméthoxysilane, l'allylméthyldichlorosilane, l'allyldiméthylchlorosilane, l'allyldiméthoxysilane, l'allyldichlorosilane, l'allyl(chloropropyl)-dichloro-silane, l'allyl-(chlorométhyl)diméthylsilane, le 3-(n-allylamino)propyl-triméthoxysilane, le butényl-triéthoxysilane, le buténylméthyldichlorosilane, le 5-hexényl-trichlorosilane, le 5-hexényldiméthylchlorosilane, l'hexényltriéthoxysilane, le vinyltriisopropoxysilane, le vinyltris(méthoxypropoxy)silane, le vinyltris-(2-méthoxy-éthoxy)-silane, le vinyltriphénoxysilane, le vinyl-triméthoxysilane, le vinyltriéthoxysilane, le vinyl-trichlorosilane, le vinyltritertiobutoxysilane, le vinyl-triacétoxysilane, le vinyloctyldichlorosilane, le vinyl-méthyldiméthoxysilane, le vinylméthyldiéthoxysilane, le vinylméthyldichlorosilane, le vinylméthyldiacétoxysilane, le 3-cyclohexényltrichlorosilane, le [2-(3-cyclohexenyl)-éthyl]-triéthoxysilane, le méthacrylate de 3-(triméthoxy-silyl)-propyle et, de préférence, le vinyltriméthoxysilane.

8. Procédé selon l'une des revendications 1 à 7, dans lequel, après l'étape d'exposition (ii), le procédé comprend en outre l'étape (iiia) d'hydrolyse du polysulfure-polysilane (III), ladite hydrolyse étant préférentiellement une hydrolyse acide, pour former un revêtement optique (IVa).

9. Procédé selon l'une des revendications 1 à 7, dans lequel, après l'étape d'exposition (ii), le procédé comprend en outre les étapes de :

mélanger le polysulfure-polysilane (III) avec un autre silane choisi dans le groupe consistant en le Glymo, un autre polysulfure-polysilane (III) différent et leurs associations ; et
hydrolyser (iiib) le mélange pour former un revêtement optique (IVb), ladite hydrolyse étant préférentiellement une hydrolyse acide.

10. Procédé selon l'une des revendications 8 et 9, dans lequel, après l'étape d'hydrolyse (iiia) ou (iiib), le procédé comprend en outre l'étape d'addition de nanoparticules fabriquées à partir d'un ou plusieurs oxydes inorganiques au revêtement optique (IVa) ou (IVb), les nanoparticules comprenant de préférence de 20 % à 80 % du poids du revêtement optique (IVa) ou (IVb).

11. Procédé selon l'une des revendications 1 à 7, dans lequel, après l'étape d'exposition (ii), le procédé comprend en outre les étapes de :

à hydrolyser (iv) le polysulfure-polysilane (III) ; et
à concentrer et ensuite chauffer la matière hydrolysée pour former une matière en masse (V).

12. Procédé selon la revendication précédente, dans lequel, après ladite étape d'hydrolyse (iv), le procédé comprend en outre l'étape d'addition d'un catalyseur choisi dans le groupe comprenant des chélates métalliques et des amines.

13. Polysulfure-polysilane (III) pouvant être obtenu par un procédé selon l'une des revendications 1 à 12, et ayant de préférence un indice de réfraction dans l'intervalle de 1,47 à 1,55.

14. Revêtement optique (IVa, IVb) obtenu par hydrolyse du polysulfure-polysilane (III) de la revendication 13, dans lequel, de préférence, ledit revêtement optique (IVa, IVb) comprend des nanoparticules d'un ou plusieurs oxydes inorganiques, de préférence dans l'intervalle de 20 % à 80 % du poids du revêtement optique (IVa, IVb).

15. Matière en masse (V) obtenue en hydrolysant, en concentrant et ensuite en chauffant le polysulfure-polysilane (III) de la revendication 14.

16. Article optique, de préférence lentille optique, fabriqué à partir d'une matière de substrat de lentille et revêtu d'un revêtement optique selon la revendication 14.

17. Article optique, de préférence lentille optique, fabriqué à partir de la matière en masse (V) selon la revendication 15.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 1785458 A **[0004]**
- US 20050123771 A **[0005]**
- US 2003165698 A **[0005]**
- US 6624237 B **[0007] [0038] [0051] [0052]**
- WO 9425406 A **[0007]**